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Computer Modelling of Microporous Materials
C.R.A. Catlow, R.A. van Santen and B. Smit (editors)

Chapter 2

Adsorption phenomena in microporous materials

B. Smit*

Department of Chemical Engineering, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

1. Introduction

In this chapter, the first of three examining the application of simulation technique to the study of sorbed molecules in zeolites, we focus on the use of Monte Carlo simulations to study the adsorption in zeolites. We concentrate on those systems for which the conventional molecular simulation techniques, molecular dynamics, and Monte Carlo, are not sufficiently efficient. In particular, to simulate the adsorption of long-chain hydrocarbons novel Monte Carlo techniques have been developed. Here we discuss configurational-bias Monte Carlo (CBMC) which has been developed to compute the thermodynamic properties. The use of these methods is illustrated with some examples of technological importance.

The fact that the sorption behavior of molecules depends on the details of the structure of a microporous material is the basis of many applications of these materials. Therefore, it is important to have some elementary knowledge on the number of molecules that are adsorbed at a given condition. In fact, many monographs and review articles have been written on these adsorption phenomena [1–3]. Yet, our understanding of the sorption behavior is far from complete. Most experiments yield important macroscopic data, for example, heats of adsorption or adsorption isotherms, from which one can only indirectly extract molecular information on these adsorbed molecules.

*E-mail: b.smit@science.uva.nl

Compared to pure component adsorption our knowledge on competitive adsorption in mixtures is very poor. Yet, most applications involves mixtures. As a consequence most of the experimental data on these applications have been analyzed with incomplete data on the number of molecules that are adsorbed. In addition, even if one would have all pure component adsorption data available, the number of mixtures one could form with these pure components is simply too large to handle. Therefore, the probability is very small that the literature gives an answer to a question related to the number of molecules of a particular component that are adsorbed at a given pressure and temperature in a given microporous material. It is therefore important to have reliable theoretical methods that allow us to approximate the sorption behavior.

In this review we will illustrate the importance of detailed knowledge of the sorption behavior to understand better the properties of the system. The monograph of Ruthven [1] contains an excellent summary of the experimental techniques to measure adsorption isotherms and theoretical methods to analyze these experimental data. Over the last few years molecular simulation techniques have become an attractive alternative to study the sorption in microporous materials. In this work we focus on the applications of these simulation techniques upon. Therefore, it is important to emphasize that although in the examples the sorption behavior has been studied using molecular simulations, this is however, not essential. Similar results could have been obtained from experiments, but for these types of systems only simulation results are available. Some details on the simulation techniques that are used to study the adsorption of molecules in microporous materials are discussed in the next section. Additional information on the computational aspects of adsorption of molecules in zeolites are given in the review by Fuchs and Cheetham [4] and on diffusion aspects in a review by Demontis and Suffritti [5].

2. Molecular simulations

Several molecular simulation techniques have been used to study the adsorption in zeolites. The earlier studies used Molecular Mechanics to study the conformation or docking of molecules. From a computational point of view such simulations are relatively simple since they only involve the conformation of the molecule with the lowest energy. From a Statistical Thermodynamics point of view such a conformation corresponds to the equilibrium distribution at $T=0$ K, where entropy

effects do not play a role. All applications of zeolites, however, are at elevated temperatures. Simulations at these conditions require the use of molecular dynamics or Monte Carlo techniques. For such simulations one needs to sample many million configurations, which does require much more CPU time.

Because of the CPU requirement most of the systems that have been studied by Monte Carlo techniques and molecular dynamics concern the adsorption of noble gases or methane. Only a few studies of ethane or propane have been published. Only very recently the computers have become sufficiently powerful to perform molecular dynamics simulations of long-chain alkanes [6,7]. The reason why only small molecules have been studied becomes clear from the work of June et al. [8], in which molecular dynamics was used to investigate the diffusion of butane and hexane in the zeolite silicalite. June et al. showed that the diffusion of butane from one channel of the zeolite into another channel is very slow compared to diffusion of bulk butane. As a consequence many hours of computer time were required to obtain reliable results. In addition, the diffusion decreases significantly with increasing chain length.

The above example illustrates the fundamental problem of molecular dynamics. In a molecular dynamics simulation the approach is to mimic the behavior of the molecules as good as possible. If successful, all properties will be like in nature, including the diffusion. If the molecules diffuse slowly this will be reflected in very long simulation times and in the case of long-chain alkanes these simulation times can only recently be reached.

In principle, one can circumvent this intrinsically slow dynamics by using a Monte Carlo technique. In a Monte Carlo simulation one does not have to follow the 'natural path' and one can, for example, perform a move in which it is attempted to displace a molecule to a random position in the zeolite. If such a move is accepted, it corresponds to a very large jump in phase space. Again, utilization of such type of 'unnatural' Monte Carlo moves turned out to be limited to small molecules as is shown in the next section.

2.1. Monte Carlo simulation of adsorption

It may not be obvious why we need efficient Monte Carlo methods to simulate chain molecules. In general, a molecular dynamics approach is much easier to generalize to complex molecules. An example of an experiment that is 'impossible' to simulate using molecular dynamics is the computation of an adsorption isotherm.

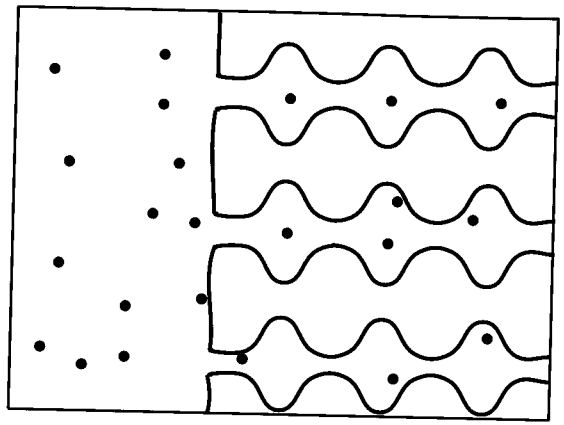

Fig. 1. A zeolite in direct contact with a gas, equilibrium is obtained via the diffusion of molecules from the gas phase into the zeolite.

Experimentally, one measures, for example, the weight increase of a zeolite sample as a function of the external pressure. In a simulation we can mimic this experimental setup (see Fig. 1); one needs a reservoir that is in open contact with a zeolite. For long-chain hydrocarbons the equilibration in the laboratory may take hours or even several days. It would be very impractical to simulate this experiment with a simulation. Even if one would have the patience to wait several million years before our computer experiment is equilibrated, one has to worry about the zeolite surface and one has to simulate a large reservoir of uninteresting molecules. It is therefore much more convenient to perform a grand-canonical Monte Carlo simulation (see Fig. 2). In such a simulation one imposes the temperature and chemical potential and computes the average number of particles in the (periodically) repeated zeolite crystal. It is important to note that in such a simulation the number of particles is not fixed but varies during the simulation. In such a simulation one therefore has to perform Monte Carlo moves which attempt to add or to remove particles.

For small absorbents such as methane or the noble gases, convention grand-canonical Monte Carlo simulations can be applied to calculate the adsorption isotherms in the various zeolites [9–15]. An example of an adsorption isotherm of methane in the zeolite silicalite is shown in Fig. 3. These calculations are based on the model of Goodbody et al. [11]. The agreement with the experimental data is very good, which shows that for these well-characterized systems simulations can give data that are comparable with experiments.

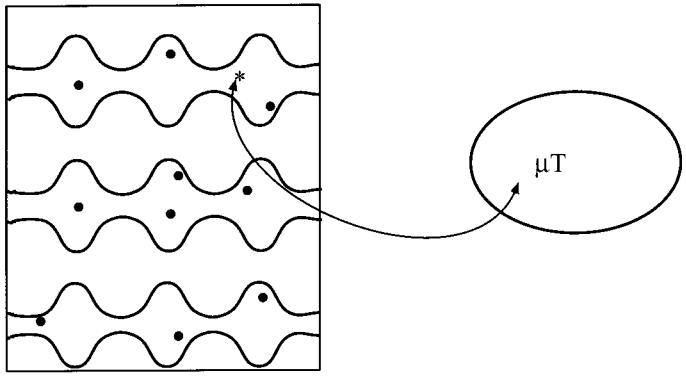

Fig. 2. Grand-canonical Monte Carlo; a zeolite in indirect contact with a reservoir, which imposes the chemical potential and temperature by exchanging particles and energy.

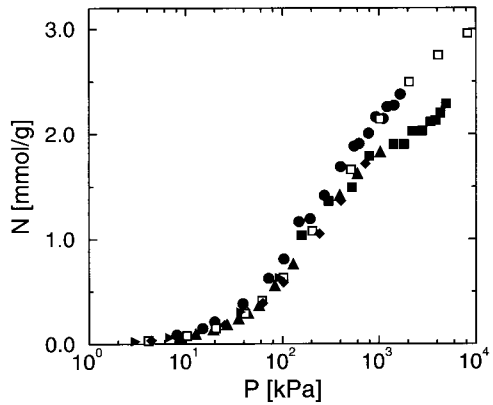

Fig. 3. Adsorption isotherms of methane in silicalite, showing the amount of methane adsorbed as a function of the external pressure. The black symbols are experimental data (see Ref. [16] for details). The open squares are the results of grand-canonical simulations using the model of Ref. [11].

In these simulations an attempt to insert a molecule is performed by generating a random position in the zeolite. If this position overlaps with one of the zeolite atoms the probability is high that such an attempt is rejected. The success of such a simulation depends on the number of successful attempts to insert a particle. To apply such a simulation for a long-chain alkane, one has to be able to insert such a molecule in a zeolite. In such a simulation one can observe that out of the 1000 attempts to move a methane molecule to a random position in

the zeolite 999 attempts will be rejected because the methane molecule overlaps with a zeolite atom. If we were to perform a similar move with an ethane molecule, we would need 1000×1000 attempts to have one that was successful. Clearly, this random insertion scheme will break down for any but the smallest alkanes.

2.2. *Monte Carlo simulations of chain molecules*

2.2.1. *Configurational-bias Monte Carlo*

To make Monte Carlo simulations of long-chain molecules possible the configurational-bias Monte Carlo (CBMC) technique was developed [17]. The principle idea of the CBMC technique is to grow a molecule atom by atom instead of attempting to insert the entire molecule at random. Figure 4 shows one of the steps in this algorithm. Important to note is that this growing procedure introduces a bias, such that only the most favorable configurations are being generated. If one were to use the ordinary Metropolis acceptance rule, such a bias in the configurations of the molecules would lead to an incorrect distribution of configurations. This bias can be removed exactly by adjusting the acceptance rules [17].

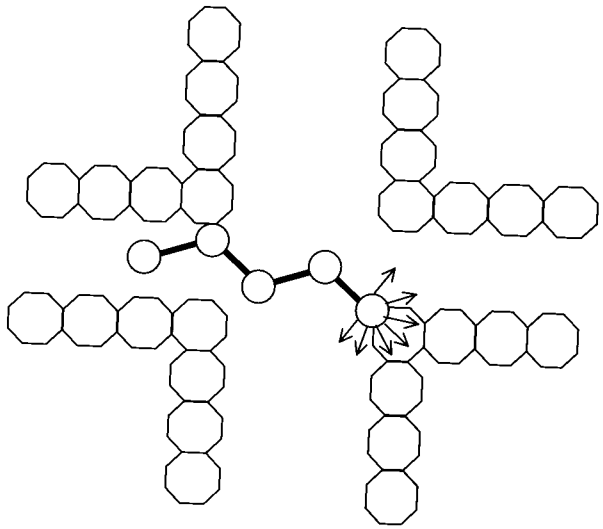

Fig. 4. Schematic drawing of the growing of an alkane in a zeolite in a CBMC move. The octagons represent the atoms of the zeolite and the circles represent the atoms of the alkane. Four atoms have been inserted successfully, and an attempt is made to insert the fifth.

It is not the purpose of this review to give an extensive discussion on the implementation of this algorithm for the adsorption of linear and branched alkanes in zeolites; details can be found in Refs. [18,19]. Smit and Siepmann estimated that for the adsorption of dodecane in silicalite a CBMC simulation can be up to 10–20 orders of magnitude (!) more efficient than the conventional techniques [20].

2.2.2. *Free-energy calculation*

In the CBMC algorithm the Rosenbluth scheme is used to generate new conformations of the hydrocarbons. This method can also be used to compute the free energy of chain molecule in a zeolite. At infinite dilution this free energy is related to the Henry coefficient. In this scheme a molecule is grown atom by atom using the algorithm of Rosenbluth and Rosenbluth [21]. During the growing of an atom several trial positions are probed; of each of these positions the energy is calculated, and the one with the lowest energy is selected with the highest probability according to:

$$p_i(j) = \frac{\exp[-\beta u_i(j)]}{\sum_{l=1}^{k} \exp[-\beta u_i(l)]} = \frac{\exp[-\beta u_i(j)]}{w(i)},$$

where $u_i(l)$ is the energy of atom i at trial position l. When the entire chain is grown, the normalized Rosenbluth factor of the molecule in configuration Γ can be computed:

$$\mathcal{W}(\Gamma) = \prod_{i=1}^{l} w(i)/k.$$

In Ref. [17] it is shown that the average Rosenbluth factor is related to the chemical potential of the molecule:

$$\langle \exp(-\beta u) \rangle = \mathcal{C}\langle \mathcal{W} \rangle,$$

where $\mathcal{C}$ is a constant defining the reference chemical potential (see Ref. [17] for more details).

These free-energy calculations can be used to compute the Henry coefficient. If the external pressures of interest are sufficiently low, a good estimate of the adsorption isotherm can be obtained from the

Henry coefficient K_H. Under these conditions, the number of adsorbed molecules per unit volume (ρ_a) is proportional to the Henry coefficient and external pressure P:

$$\rho_a = K_H P.$$

The Henry coefficient is directly related to the excess chemical potential of the adsorbed molecules. To see this, consider the ensemble average of the average density in a porous medium. In the grand-canonical ensemble, this ensemble average is given by

$$\left\langle \frac{N}{V} \right\rangle = \frac{1}{Q} \sum_{N=0}^{\infty} \frac{q(T)^N V^N \exp(\beta\mu N)}{N!} \int ds^N \exp[-\beta \mathcal{U}(s^N)] N/V$$

$$= \frac{q(T)\exp(\beta\mu)}{Q} \sum_{N=0}^{\infty} (q(T)V)^{N-1} \exp[\beta\mu(N-1)]/(N-1)!$$

$$\times \int ds^{N-1} \exp\left[-\beta \mathcal{U}(s^{N-1})\right] \int ds_N \exp[-\beta \mathcal{U}(s_N)]$$

$$= q(T)\exp(\beta\mu)\langle \exp(-\beta \Delta \mathcal{U}^+) \rangle,$$

where $\Delta \mathcal{U}^+$ is defined as the energy of a test particle and $q(T)$ is the kinetic contribution to the molecular partition function. In the limit $P \to 0$, the reservoir can be considered an ideal gas

$$\beta\mu = \ln\left(\frac{\beta P}{q(T)}\right).$$

Substitution of this equation gives

$$\exp(\beta\mu^{ex}) = \langle \exp(-\beta \Delta \mathcal{U}^+) \rangle = \frac{\langle N/V \rangle}{\beta P}.$$

This gives, for the Henry coefficient,

$$K_H = \beta \exp(-\beta\mu^{ex}).$$

2.3. Intermolecular potentials

In the previous section simulation techniques are discussed that allow us to compute adsorption isotherms. The input of such a simulation is the intermolecular potentials.

Most simulations start with the assumption of Kisilev and co-workers [22] that the zeolite crystal is rigid. The atomic positions can be taken from the X-ray diffraction. For most structures the atomic data are published on the Web [23]. From a computational point of view the use of a rigid zeolite is very attractive. Since the zeolite atoms do not participate in the simulation, the total number of atoms for which the force has to be computed is reduced significantly. In addition, the potential energy at a given point inside the zeolite can be calculated a priori. If this is done for points on a grid, the potential energy at an arbitrary point can be estimated from interpolation during the simulations [24,25]. With such an interpolation scheme a gain in cpu-time of one to two orders of magnitude can be gained.

In some studies the importance of a flexible zeolite structure is emphasized [26,27]. It can be expected that framework flexibility can be of importance for the modeling of the diffusion of the molecules, since a flexible framework may reduce the diffusion barriers. Since these barriers correspond to positions in which the molecules have a relatively high energy and therefore do not contribute much to the equilibrium properties, it can be expected that the assumption of a rigid zeolite lattice is less severe for these properties. Important to note is that the adsorption of molecules may induce structural transitions of the zeolite lattice [28].

Some zeolites can be synthesized in the all-silica form. In practice, however, the none all-silica zeolites are very important. For example, zeolites are made catalytically active by substitution of trivalent aluminum for tetravalent silicon into the framework. This introduces chemical disorder which has to be taken into account in the simulations.

If we assume an all-silica structure and consider the adsorption of nonpolar molecules, for example alkanes, it is reasonable to assume that the alkane–zeolite interactions are dominated by dispersive forces, which are described with a Lennard-Jones potential

$$U(r_{ij}) = \begin{cases} 4\varepsilon_{ij}[(\sigma_{ij}/r_{ij})^{12} - (\sigma_{ij}/r_{ij})^6] & r_{ij} \le R_c \\ 0 & r_{ij} > R_c \end{cases},$$

where r_{ij} is the distance between atoms i and j, ε is the energy parameter, σ is the size parameter, and R_c is the cut-off radius of the potential. The contribution of the atoms beyond the cut-off to the total energy is estimated using the usual tail corrections [29]. Since the size as well as the polarizability of the Si-atoms are much smaller than those of the O-atoms of the zeolite, one can assume that the contributions of these Si-atoms can be accounted for by using effective interactions with the O-atoms.

In many studies the adsorbed molecules are modeled as united atoms, for example, in case of an alkane the CH_4, CH_3, and CH_2 groups are considered a single interaction center. Despite the simplification these models do very well in reproducing the thermodynamic data of liquid hydrocarbons [30]. Also here one has to keep in mind that such a model has its limitations. For example, it is well known that a united atom model of an alkane cannot reproduce the experimental crystal structure. Details on the parameters of the various models can be found in Ref. [19].

With the above assumption the zeolite–alkane interactions are reduced to finding the optimal Lennard-Jones parameters between the oxygen of the zeolite and the united atoms of the alkane. Because of this assumption it is very difficult to use, for example, quantum chemical calculations to systematically develop methods to compute interaction parameters. The assumption that are being made are very specific for zeolites and therefore difficult to transfer methods that have been developed to generate interaction parameters to these systems. Therefore, most models are obtained by fitting to some experimental data [16].

For zeolites that contain aluminum two additional aspects have to be addressed. One aspect is the position of the aluminum atoms in the zeolite framework and the counterions to compensate for the charge deficit. The question where the aluminum positions are in a certain zeolite has been addressed by many researchers, but is far from being solved. It is beyond the scope of this review to give a detailed discussion on the various methods that are employed to determine the location of the Al atoms. Three approaches appear in the literature. To assume that the net positive charge is distributed over all T-sites, i.e. no distinction between Si and Al atom is made but both are considered as a single T-site. For some zeolites and for some specific Si/Al, the position of the Al atoms can be obtained from the crystal structure. Finally, theoretical methods have been developed to assign the Al atoms using semiempirical rules (see Ref. [31] for more details). The exact location of the Al atoms has important consequences for the preferred

location of the cations. It is reasonable to assume that, unless the temperature is very high, the cations prefer to be close to the Al atoms. Therefore, important information on the location of the Al atoms is also contained in the location of the cations. Mellot-Draznieks et al. [32] studied the cation distribution in NaX faujasite using a model in which the charge was uniformly distributed of the T-sites [33] with a method in which an explicit distinction between the Al and Si sites was made. The conclusion of this study was that the uniform distribution gave a reasonable prediction of the location of the cations, but to obtain a correct location of the sodium ions in the supercages a more detailed model was required.

The presence of the counterions implies for adsorption studies that additional intermolecular potentials have to be introduced to take into account the interactions of the adsorbed molecules with these ions and the ions with the zeolite framework [34].

3. Adsorption isotherms

From a practical point of view it is important to have information on the number of molecules adsorbed in the pores of the zeolite as a function of the gas pressure. Here we illustrate how molecular simulation can give us some molecular insights in some special features of these adsorption isotherms.

3.1. Pure components

Most of the simulation studies investigate the energetics, siting, or diffusion of the adsorbed molecules and only a few results on the simulation of isotherms have been reported. An overview on the pure component adsorption that has been studied using molecular simulation has been compiled by Fuchs and Cheetham [4]. The early work on the simulation of adsorption isotherms was focused on small molecules such as noble gases or methane (see Fig. 3 for a typical example) [9,10,12,14,35–37] or mixtures of these gases [13,15,36].

At low pressures the adsorption can be computed from the Henry coefficient. For example, Maginn et al. [38] and Smit and Siepmann [20,25] used the approach described in the previous section to compute the Henry coefficients of linear alkanes adsorbed in the zeolite silicalite. Since the Henry coefficient is calculated at infinite dilution, there are no intramolecular alkane–alkane interactions. In Fig. 5 the Henry coefficients of the *n*-alkanes in silicalite as calculated by Smit

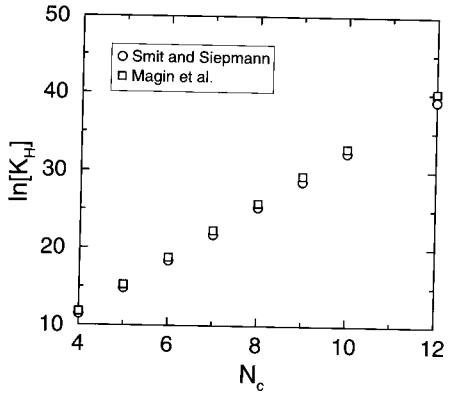

Fig. 5. Henry coefficients K_H of *n*-alkanes in the zeolite silicalite as a function of the number of carbon atoms N_c, as calculated by Maginn et al. [38] and Smit and Siepmann [25].

and Siepmann are compared with those of Maginn et al. If we take into account that the models considered by Maginn et al. and Smit and Siepmann are slightly different, the results of these two independent studies are in very good agreement.

Knowledge on the adsorption of pure components in zeolites is not only of practical importance but also of scientific interest since steps or kinks in the adsorption curve may signal transitions occurring in the pores of the zeolite. A typical example of this behavior is the adsorption of methane in $AlPO_4$-5 (AFI). Experimentally, one can find two steps in the adsorption isotherm at $T=77$ K [39]. One step at a loading of approximately four molecules per unit cell and another step at a loading of six molecules per unit cell. These steps are also found via molecular simulations [40,41]. Simulations predict that these steps should disappear if the temperature is raised above $T=100$ K, suggesting a phase transition to occur in the pores of the zeolite.

The adsorption isotherms of branched alkanes in silicalite also show a step for a given number of molecules per unit cell (see Fig. 6). Such a step is not observed for the linear isomers. For these branched molecules the steps are explained in terms of a preferential siting of these molecules at the intersections of the linear and zig-zag channels. Figure 6 shows that for isobutane a plateau is formed for four molecules per unit cell. There are four intersections per unit cell and the branched alkanes first adsorb at these sites. Once all intersections are occupied, the next atom has to adsorb in between two intersections. Since these sites are less favorable for the bulky branched molecules, this requires much higher pressure before these other sites are occupied.

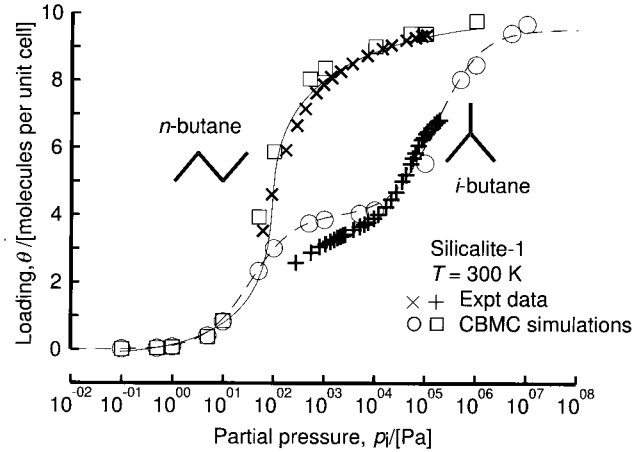

Fig. 6. Sorption isotherms for normal and isobutane at 300 K. Comparison of CBMC simulations with experiments. The data are taken from Ref. [42].

Figure 6 also shows a comparison of simulated and experimental adsorption isotherms of linear and branched alkanes in the zeolite silicalite. The simulations give a nearly quantitative description of the experimental adsorption isotherms. Also for other alkanes in silicalite a similar agreement has been obtained [19]; the simulations reproduce all qualitative features found in the experiments.

The good agreement of the simulated adsorption isotherms of the linear and branched hydrocarbons with the experimental ones is an encouraging result. Experimental adsorption isotherms are not readily available for a given zeolite at a given condition. These results show that one can get a reasonable estimate from a molecular simulation. However, it is important to point out that most simulations have been performed for silicalite for which the potentials have been developed as well. Unfortunately, there are not many experimental adsorption isotherms of other all-silica zeolites. It is therefore not known how accurate these simulations extrapolate to other zeolites.

At this point it is important to mention that these simulations use a rigid zeolite lattice. To see the limitation of this assumption, let us consider the transition, which is observed in the adsorption of benzene or xylene isomers in silicalite [43–45]. Olsen et al. [43] observed a step in the adsorption isotherm for *p*-xylene at 70°C, a plateau at a loading of four molecules per unit cell with a saturation at six molecules per unit cell (see Fig. 7). van Koningsveld showed that four molecules per unit cell in a structural transition of the zeolite framework from the *ortho* to the *para* structure occur [44].

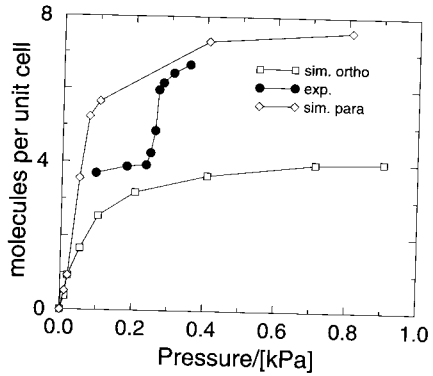

Fig. 7. Comparison of the simulated (open symbols) and experimental adsorption isotherms of *p*-xylene in silicalite. The simulation use the *para* and *ortho* structure of silicalite, and the simulation results are taken from Ref. [46]. The experimental data are taken from Ref. [43].

From a molecular simulation point of view this is a very challenging system to study. Most simulation studies use a rigid zeolite structure. For molecules that do not have a tight fit in the zeolite framework, this appears to be a good assumption. In the case of aromatics in silicalite the fit is very tight and can even induce a phase transition. The differences between the *ortho* and the *para* structure of silicalite are relatively small, yet these small differences result in very different adsorption behavior. Snurr et al. [46] have computed the adsorption isotherms of *p*-xylene in both the *ortho* and the *para* structure of silicalite (see Fig. 7). For both the *ortho* and the *para* structure a simple Langmuir isotherm is observed. The maximum loading for the *ortho* and the *para* structure was four and eight molecules per unit cell, respectively. Comparison with the experimental data shows that the jump in the adsorption isotherm is consistent with a change in the structure.

A similar behavior phase transition was observed for the adsorption of benzene in silicalite [47]. For this system, however, the agreement between experiments and the simulations of Snurr et al. was good at high temperatures but less satisfactory at low temperatures. This discrepancy motivated Clark and Snurr [48] to study the adsorption of benzene in silicalite in detail. Their study showed that the adsorption isotherms of benzene are very sensitive for small changes in the structure of the zeolite. Also these calculations were performed with a rigid zeolite and one would expect that the zeolite structure would 'respond' to the presence of these molecules. Clark and Snurr point out

that this requires simulation with a model of a zeolite with accurate flexible lattice potentials.

3.2. Mixtures

Most experimental techniques to determine adsorption isotherms are based on measuring the weight increase of the zeolite due to the adsorption of molecules. For a pure component this directly relates to the number of adsorbed molecules, but for a mixture additional experiments are required to analyze the composition of the adsorbed molecules. As a consequence far less experimental data on mixtures are available.

From a practical point of view the separation of xylene isomers using zeolites is an important system. Lachet et al. [49,50] used molecular simulations to study the effect of cations on the adsorption selectivity. The simulations showed a reversal of the selectivity if Na^+ is exchanged by K^+. The differences in selectivity are related to a combination of differences in size and location of the cations which results in a completely different adsorption behavior.

For the mixtures of small hydrocarbons, adsorption isotherms have been obtained by Dunne et al. [51] and Abdul-Rehman [52]. These mixture isotherms can be reproduced using molecular simulations [53,54]. For these small molecules the observed adsorption behavior is consistent with the theoretical calculations of Talbot [55], in which it is shown that for a mixture of molecules, because of entropic reasons, the smallest component at sufficiently high pressures absorbs better than the bigger components. For mixtures of linear and branched alkanes the situation is more complex. For example, Vlugt et al. [19] have shown that for a mixture of *n*-hexane and 3-methyl pentane in silicalite *n*-hexane is preferentially adsorbed at sufficiently high pressures (see Fig. 8). More complex mixture of linear, mono- and di-branched hydrocarbons have been studied by Calero et al. [56]. These simulations show that, due to configurational entropy effects, in a mixture of mono- and di-branched isomers at sufficiently high pressure the mono-branched isomers are preferentially adsorbed in silicalite.

4. Applications

In this section we illustrate the use of adsorption data to explain some experimental observations in zeolites. The interesting aspect is that at

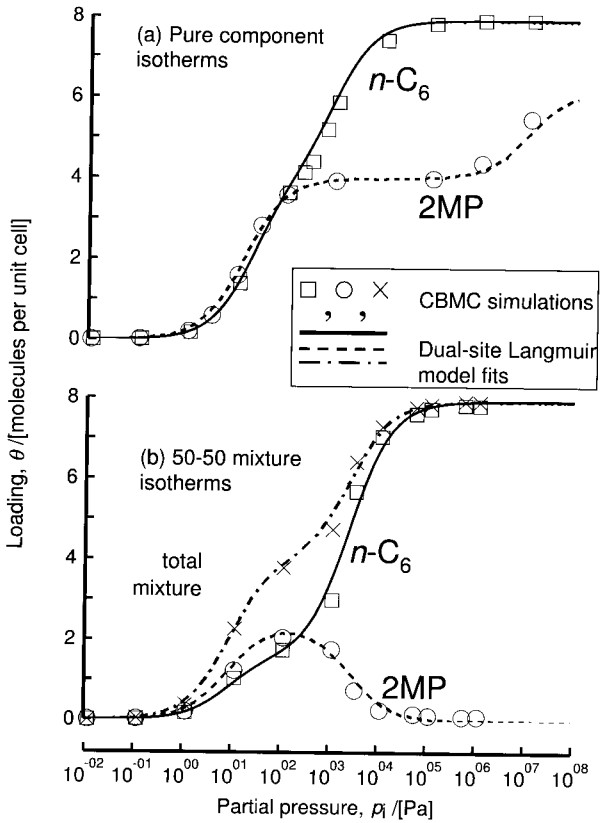

Fig. 8. Configurational-bias Monte Carlo simulations of the adsorption isotherms of *n*-hexane and 2-methyl pentane at $T = 300$ K [19]. The lines are fits to the dual-site Langmuir isotherm model.

first sight it may not be obvious that the explanation is related to adsorption phenomena.

4.1. Permeation through membranes

A description of the permeation through membranes requires the knowledge of the fluxes as a function of the concentration of the molecules. Krishna and Wesselingh [57] have shown that the fluxes can be described using the Maxwell–Stefan equation, which relates the fluxes to the diffusion coefficients and the gradient of the chemical potential. This relation tells us that we need to know the chemical potential as a function of the loading of the molecules in a zeolite. To be more precise one needs to know the loading of each individual

component. For pure components there are not many experimental adsorption isotherms, for mixtures it is even worse. Therefore, most estimations of the permeation are based on experimental Henry coefficients of the pure components. These Henry coefficients show the 'expected' temperature dependence, and therefore any anomalous behavior is often attributed to a dependence of the diffusion coefficients on temperature or pressure.

To compute the Maxwell–Stefan diffusion coefficient or Darken-corrected diffusion coefficient, from the experimentally measured fluxes (or Fick diffusion coefficient), one has to convert a gradient in the concentration to a gradient in the chemical potential. To be able to make this conversion one has to know the adsorption isotherms. For a normal Langmuir isotherm an increase of the chemical potential (or pressure) results in an increase in the concentration inside the pores of the zeolite. However, if one approaches maximum loading an increase in the pressure hardly increases the loading, which results in a large Darken correction. In the previous section, we have seen that the adsorption isotherm of benzene in silicalite (at 30°C) shows a step at four molecules per unit cell. Such a step has consequences for the diffusion since a large thermodynamic (Darken) correction can also be expected at the plateau of the adsorption isotherm. This results in a nonmonotonic dependence of the Fick diffusion coefficient as a function of the loading [58]. The Maxwell–Stefan diffusion coefficient is nearly independent of the loading. The practical importance of this result is that if the adsorption isotherm of the system is known, a much better estimation of the (Fick) diffusion coefficient as a function of loading can be made.

For some of the pure components the adsorption isotherms have been determined experimentally. For mixtures, however, far less is known. It would therefore be interesting to investigate how well one can approximate the mixture isotherm using pure component data. In Fig. 8 the pure component isotherms and a mixture isotherm for a mixture of linear and branded isomers are shown. At low pressures the adsorption isotherm is simply the sum of the pure component isotherms. At elevated pressures, however, one observed that the branched alkane is expelled from the zeolite. Also here such a nonmonotonic dependence of the adsorption of the components as a function of the pressure has its consequences for the diffusion. For the permeation through a membrane of the mixture of these components, thermodynamic contributions to the diffusivity results in an enhancement of the selectivity by a factor of 20 compared to what one can predict on the basis of the pure components. In fact, these observations indicate that such

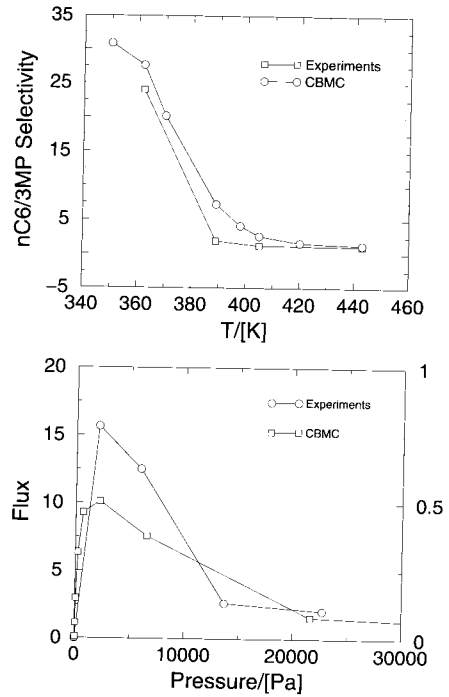

Fig. 9. Effect of temperature and pressure on selectivity or fluxes of the membrane. In the top figure the experimental data are taken from Ref. [60] and in the bottom figure from Ref. [62] and the CBMC simulations from Ref. [61].

mixture effects can be used for a novel concept to separate mixtures of hydrocarbons [59].

In Fig. 9 the temperature and pressure dependence of the selectivity of a zeolite membrane is shown. Funke et al. [60] found a sharp decrease of the selectivity when the temperature was increased above 380 K. The comparison with the simulation results, as obtained from the adsorption isotherms [61], show that this temperature dependence can be explained in terms of differences in adsorption. A similar explanation exists for the effect of pressure as observed by Gump et al. [62]. The maximum in the selectivity can be related to loading [61], which can be obtained from molecular simulations.

4.2. Compensation effect in zeolite catalysis

Haag [63] was among the first to realize the importance of understanding the adsorption behavior for the interpretation of catalytic

data. A famous example is the 'compensation effect'. The reaction rate constants of the cracking of *n*-paraffins as a function of carbon number show a higher activation energy which is compensated by an increase of the exponential factor. However, detailed calculations on the reaction mechanism do not support an increase of the activation energy for longer carbon chains. Haag showed that the kinetic data were analyzed using the gas-phase concentration and did not take into account differences in adsorption, i.e. at a given pressure the number of adsorbed molecules in the pores depends on the carbon number. Haag showed that if the kinetic data are corrected for these differences in number of adsorbed molecules, he obtained a constant activation energy.

The ideas of Haag were used by Maesen and co-workers [64,65] to explain shape selectivity of hydroconversion reactions in zeolites. Maesen and co-workers computed the free energy of various reaction intermediates in the pores of the zeolite. It is argued that those intermediates with the lowest free energy are preferentially formed in the pores of the zeolite. Whereas for the large-pore zeolites the zeolite structure has little influence on the thermodynamics, for the small pore zeolite pronounced effects are observed. An important aspect is that some of these reaction intermediates are favored because they have a structure that is commensurate with the zeolite. Some intermediates form inside the pores of a zeolite but are too bulky to diffuse out of the zeolite. Yet, the products that originate from such intermediates can be observed in the product distribution.

Figure 10 shows the contribution of the free energy for various reaction intermediates of a hydroconversion reaction of *n*-decane. In a large-pore zeolite (FAU) all reaction intermediates can form and the zeolite contributes little to the relative free energies of formation. In a small-pore zeolite (TON), however, comparison of the various free energies of formation shows that in TON the formation of the large tri- and di-branched intermediates are suppressed. The zeolite MFI and MEL are very similar, yet there is a marked difference in the free energy of formation of 2,4-dimethyloctane and 4,4-dimethyloctane. Schenk et al. argue that these differences explain the differences in the experimental product distribution.

In the approach of Maesen and co-workers it is assumed that the shape selectivity is determined by the 'stable' reaction intermediates. In fact, they assume that the Polanyi–Bronsted principle holds. This implies that for a given reaction where there are competing paths to various stable reaction intermediates, if a particular reaction intermediate is favored, the zeolite lowers its free energy of formation. The

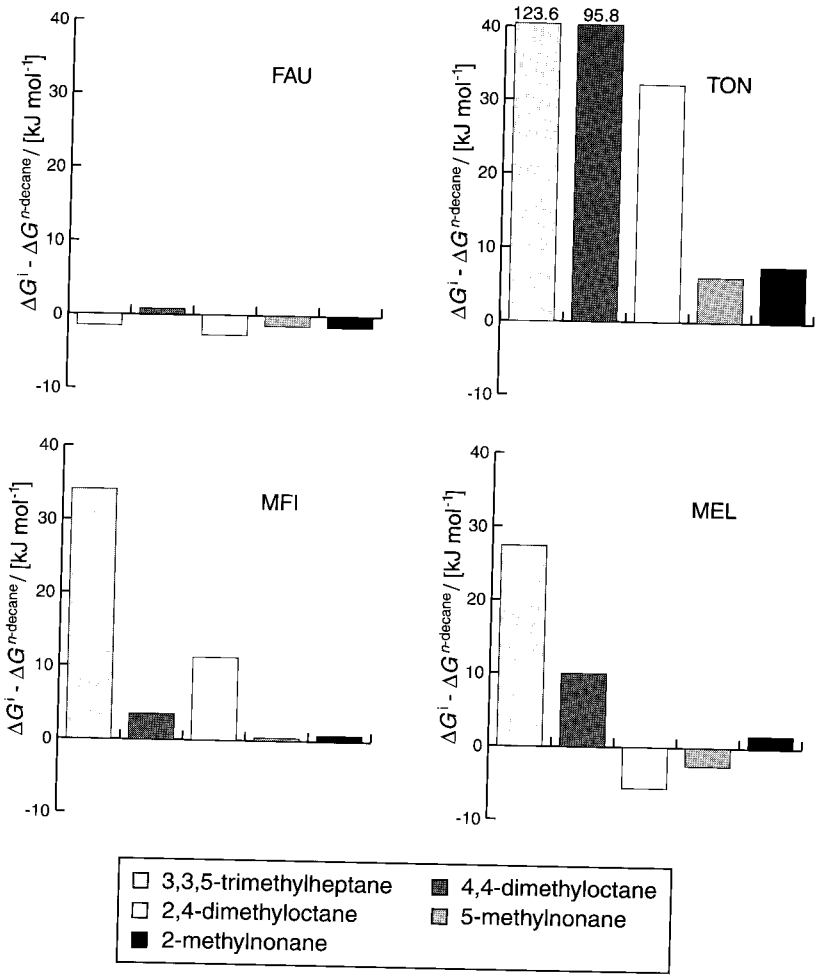

Fig. 10. The Gibbs free energy of formation of hydrocarbons relative to decane in the zeolites FAU, TON, MFI, and MEL as obtained from CBMC simulations [65].

Polanyi–Bronsted principle implies that a similar shift of the free energy of the transition state associated with this particular path can be expected. This approach will therefore fail, if in a particular competing reaction path the free energy of the corresponding transition state does not follow the same trend as its product. The specific effects of confinement on the transition state has been studied by Macedonia and Maginn [66]. In this work the free energy of a transition state in a zeolite is computed assuming that this free energy is dominated by 'classical' interactions, i.e. this free energy is dominated by steric effects rather than electronic effects.

5. Concluding remarks

In this review the focus has been on the use of modern simulation techniques to compute adsorption isotherms. It is shown that for hydrocarbons in zeolite good results can be obtained. However, most of the force fields used in these studies have been developed for the zeolite silicalite. For this zeolite ample experimental data is available. It remains to be seen whether the results extrapolate equally well to other zeolites.

Linear and branched paraffins fit loosely in the channels of silicalite. Small errors in the potential related to the parameters of the potential, the positions of the zeolite atoms, or the assumption of a rigid zeolite lattice can be compensated by the use of effective potentials. For tight-fitting molecules, such as the aromatics, such an effective potential is far less successful. Hence, for such systems it is essential to further investigate the role of lattice vibrations on the adsorption. This, however, requires accurate potentials for the zeolite–zeolite interactions.

Despite the fact that the simulations do not give a perfect prediction of the experimental adsorption isotherms and that in applications the zeolites are often far from perfect crystals, these simulation methods do allow us to obtain a reasonable estimate whether for a given application for a given zeolite whose components are adsorbed. Knowledge on the adsorption is often necessary to interpret experimental data for many applications. Here, we have used the permeation through zeolite membrane and shape selectivity as a typical example in which a detailed understanding of the sorption behavior is essential to correctly interpret the experimental results.

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